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ALUMINIUM IN FOOD

by

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PREFATORY NOTE BY THE CHIEF MEDICAL OFFICER.

To the Right Hon. Sir KINGSLEY WOOD, M.P.,
Minister of Health.

SIR,

I beg to submit the following special report by Dr. G. W. Monier-Williams, who is in charge of the Chemical Laboratory of the Ministry, on Aluminium in Food.

The use of aluminium cooking vessels has been criticised from time to time on the ground that aluminium is a toxic metal and that the small amounts which may be dissolved and find their way into food may cause illness. So persistent have been these criticisms that many people have banished aluminium ware altogether from their kitchens. Possibly, the prejudice against aluminium ware is connected with the use in some countries of alum as an ingredient of baking powder, a practice which is not countenanced in this country. Dr. Monier-Williams has collected and examined all the information available upon the subject and concludes that, while aluminium salts are undesirable as ingredients of baking powders, there is no convincing evidence that aluminium cooking vessels are harmful.

I have the honour to be,

Sir,

Your obedient Servant,

ARTHUR MACNALTLY.

Whitehall,
October, 1935.

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ALUMINIUM IN FOOD

	CONTENTS	Page
1.	Introduction	4
2.	Occurrence of aluminium in nature.	
	A. In soil	4
	B. In plants	5
	C. In food... ..	6
	D. In human and animal tissues	7
3.	Analytical methods.	
	A. General	7
	B. Determination of aluminium in foods by 8-hydroxy-quinoline	9
4.	Action of food on aluminium vessels	11
5.	Behaviour of aluminium in the body.	
	A. Solubility in gastric juice	14
	B. Evidence of absorption into blood	15
	i. Aluminium in blood	15
	ii. Anaemia	15
	iii. Excretion in urine	16
	iv. Permeability experiments	17
	v. Aluminium in organs of body	17
	C. Effect on digestive tract	18
	D. General effect on health, growth and reproduction	19
	E. Results of injection of aluminium salts into the body	21
6.	Clinical observations and experience	21
7.	Conclusions	22

ALUMINIUM IN FOOD

1. INTRODUCTION.

The presence of aluminium in food and its effect on health have at various times been subjects of controversy. The addition of alum to flour, for the purpose of arresting fermentation and renovating flour damaged by damp storage, was formerly a common fraud and was forbidden by the Bread Acts of 1822 and 1836 (3 Geo. IV, c. 106 and 6 and 7 Will. IV, c. 37). About 60 years ago sodium aluminium sulphate was introduced as the acid ingredient of commercial baking powder. Strong exception was taken by Public Analysts in this country to the sale of these powders on the ground that alum salts are gastric irritants and astringents, and several prosecutions were instituted under the Sale of Food and Drugs Act of 1875. As a result of these prosecutions alum baking powders have been superseded almost entirely by phosphate powders, and it is rare now to find alum intentionally added to food. In some countries, however, alum baking powders are still widely used and there are indications that attempts are being made to revive their sale in this country.

When cooking vessels made of aluminium were introduced about 40 or 50 years ago, they met with some criticism on the ground that aluminium might be dissolved from them and find its way into food. This criticism has lately been revived. Statements have been made that aluminium is definitely poisonous, even in small quantities, if consumed over a long period and is a cause of digestive ailments, skin diseases and even cancer. These opinions have been given wide publicity and have caused many people to give up using aluminium vessels for cooking food.

In this Report an attempt is made to collect and examine the information available upon the subject of aluminium in food, with a view to reaching some definite conclusions as to whether or not it is in any way injurious.

2. OCCURRENCE OF ALUMINIUM IN NATURE.

A. In soil.

Aluminium is, next to silicon and oxygen, the commonest constituent of the earth's crust. The various natural silicates contain about 9 to 10 per cent. of aluminium, and its proportion in the earth's crust is estimated to be between 7 and 8 per cent. Agricultural soils usually contain much less than this. In eight samples of soil collected from fields in various parts of England I found aluminium in amounts ranging from 1.1 per cent. to 5.9 per cent., calculated on the dry soil.

In fertile soils aluminium, and also iron and manganese, appear to be present almost wholly in an insoluble form. Acid soils may contain soluble salts of these metals and it is these soluble salts, particularly of aluminium, which make acid soils toxic to many

plants. (Miyake 1916, Hartwell and Pember 1918, Carr and Brewer 1923.) According to Stoklasa (1918) very small amounts of aluminium favour the germination of seeds, while larger amounts interfere with germination. In general, a concentration of 0.01 per cent. of aluminium hinders growth while 0.03 per cent. kills nearly all plants in water culture. Soluble iron and manganese are almost as toxic.

B. In plants.

Aluminium does not appear to be a general constituent of plants, although in a few plants it does occur in considerable amount. Thus the ash of certain club mosses, *Lycopodium clavatum* and *L. complanatum*, contains as much as 30 to 50 per cent. of aluminium oxide. This is present in the plants in the form of a soluble organic salt which can be extracted, and the extract used direct as a mordant in dyeing (Church 1888). Maiden and Smith (1895) have drawn attention to the occurrence of a copious deposit of basic aluminium succinate in the wood of the Australian silky oak, *Grevillea robusta*.

Stoklasa (1918) carried out extensive researches on aluminium in plants. He found that xerophytes—plants growing on dry soils—contained very little aluminium, while bog and water plants contained much more, and that it was almost wholly confined to their roots. In some water plants the ash of the roots contained 10 per cent. or more of aluminium oxide. This might be due to mechanical inclusion of soil particles in the roots, or to the cell walls not being completely impervious to aluminium in solution. The plant may be unable to keep it out and have become inured to its presence. Thus many plants which, when grown in dry soil, contain very little aluminium, take up a larger amount when grown in wet or acid soils. Certain plants will grow only in acid peaty soils and, according to Stoklasa, hydrophytes will not grow unless the soil contains traces of soluble aluminium. On the other hand if the amount of aluminium in solution rises much above 0.03 per cent. all plants, including hydrophytes, are killed. Whether aluminium, in minute amounts, is a necessary constituent of plants or exercises any essential function in their growth, is not known. Iron, which in very small amounts is probably essential to plants as a constituent of the respiratory pigment cytochrome, is likewise toxic to plant life under much the same conditions as aluminium.

The figures given by Stoklasa and others for the amount of aluminium in plants have been criticised by various workers as being too high (Lehmann 1931, Levy 1931). Faulty methods of analysis and sampling have been responsible for many erroneous results. It is difficult to remove completely all particles of dust and soil from plants, especially roots, before analysis. In over 120 analyses by Levy of plants belonging to 30 natural families

the amount of aluminium in the fresh material was, in the greater number of cases, less than 10 parts per million, and in four-fifths of the samples examined the amount was less than 30 parts per million. Levy found most of the aluminium in the leaves. She found that the outer green leaves of cabbages, lettuces, etc., contained much more aluminium than the inner blanched leaves and took this as an indication that aluminium may be connected in some way with chlorophyll, and may play a part in the metabolism of the plant. If this were so one would expect to find aluminium stored in the seeds, but the amount actually found in seeds is extremely small. A more likely explanation is that the leaves of plants present a large surface in proportion to their weight and this surface is constantly exposed to dust particles in the air. However carefully the sample is cleaned it is almost impossible to remove every particle of dust, especially if the dust has become partly incorporated in the substance of the epidermis during growth, or if the epidermis is of a waxy or sticky nature. I have found that the more carefully leaves are cleaned, even to the extent of scrubbing them with soap and water, the less is the amount of aluminium found, and have come to the conclusion that much of that found in plants by different workers is adventitious in origin, due to contamination with soil and dust.

C. In food.

Very few of the vegetables used as food contain appreciable amounts of aluminium. Langworthy and Austin (1904) collected figures from various sources but most of these earlier figures were too high. Lehmann (1931) found 2.5 to 16 parts per million in various vegetable foods, and 0.2 to 8 parts per million in animal foods. In dried foods the amounts ranged from 1.3 to 72 parts per million. These figures agree well on the whole with those given by Massatsch (1929), Underhill and Peterman (1929), Winter and Bird (1929), and Bertrand and Levy (1931). Much of the aluminium found is probably due to contamination with soil and dust. A striking instance of this is afforded by coffee beans, for which Levy gives 47 parts of aluminium per million. I found, using the method given below (p. 9), 72 parts per million in the unwashed beans, and none at all in the same sample after thorough and prolonged shaking with soap and water to remove dust. Other typical results were:—bran 4.5, rice 0.45, and lettuce leaves 0.34 parts per million.

It would appear that the amount of aluminium consumed daily with food, when this is properly cleaned, is very small indeed, of the order of 5 to 10 parts, or less, per million. Whether this is mainly in the form of aluminium silicate from unavoidable dust contamination or of organic compounds of aluminium natural to plants is difficult to say. If present as silicate it would probably pass through the stomach unchanged.

D. In human and animal tissues.

The amount of aluminium naturally present in human and animal tissues has been investigated mainly by Myers and his co-workers (1928). Myers found traces of aluminium, of the order of 1 to 2 parts per million, in all organs. Underhill and Peterman's figures are rather higher, averaging about 4 parts per million for the liver and kidney. In dogs the blood contained 2 to 3 parts and some of the organs 10 to 30 parts per million. The thyroid contained as much as 124 parts per million.

The results of other investigators (Mc.Collum 1928, Wührer 1933) tend to confirm the lower figures given by Myers. In particular Mackenzie (1932) controverts Underhill's statement as to the high aluminium content of the thyroid gland. He finds only 0.5 parts per million in pigs' and rats' thyroids.

It would seem that the amount of aluminium naturally present in human and animal tissues is extremely small.

3. ANALYTICAL METHODS.

A. General.

The accurate determination of aluminium in food and biological material is a difficult matter. The amount usually present is small and it is not easy to separate it completely from iron and other metals. In the various methods used by different workers the first step is to obtain a solution free from organic matter by heating with sulphuric and nitric or chloric acids or by ashing at a low temperature and dissolving the ash. The resulting solution contains all the metals originally present and also a certain amount of phosphoric acid derived from the organic matter which has been destroyed.

An important point arises here. It is generally found that there is a slight residue insoluble in strong acids. This residue is often neglected as being due to adventitious sand or dust in the sample. It may contain aluminium silicate derived from soil, and if the object be to ascertain the total amount of aluminium in the sample, irrespective of origin and state of combination, this insoluble residue must be fused with alkali and the resulting solution added to the main portion. It may be that by neglecting this insoluble residue a closer approximation to the aluminium naturally present in the material is obtained, but it is impossible to say how much of the extraneous aluminium derived from soil or dust may be soluble in mineral acids. Where minute amounts of the metal are in question the rational procedure is to determine the total amount present.

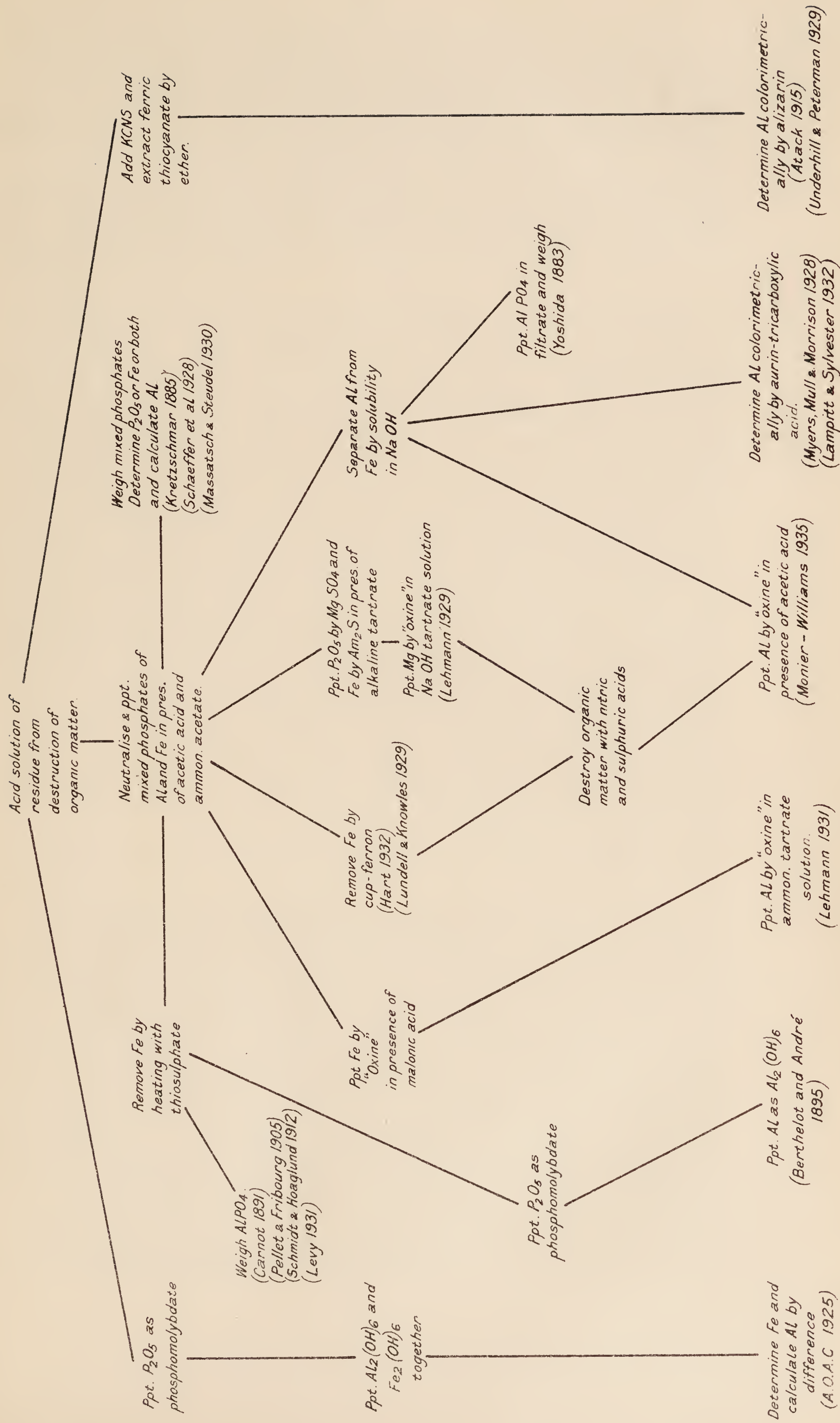
Facing page 8 the chief methods, other than spectroscopic, which have been used at various times for determining aluminium in biological material, are shewn in the form of a diagram. The salient points only are given, since it is of course impossible, in a diagram of this kind, to give details of the individual methods.


In most foods and biological material the amount of phosphoric acid in the ash is enough to combine with the greater part, if not all, of the iron and aluminium present, so that the problem in general is one of determining minute amounts of aluminium in a precipitate of mixed iron and aluminium phosphates. Methods which depend upon the estimation of aluminium in this precipitate by difference are untrustworthy. Any slight impurities which may be present have the effect of increasing the apparent amount of aluminium, and when small amounts are in question the errors may be large.

There are several ways of separating iron from aluminium in the presence of phosphoric acid. One way is to precipitate the iron by sodium hydroxide, which holds the aluminium in solution. Alternatively the mixed phosphate precipitate may be filtered off and the iron separated as basic acetate in sodium hydroxide solution. Carnot's method is to heat the mixed phosphates with sodium thiosulphate in slightly acid solution. The iron is reduced to the ferrous state and goes into solution, while aluminium phosphate is precipitated together with sulphur. Baudisch's "cup-ferron", the ammonium salt of nitroso-phenyl-hydroxylamine, has been used by one or two workers to separate iron but the cost of the reagent is against it. Iron may be precipitated by ammonium sulphide in presence of an alkaline tartrate which prevents the precipitation of aluminium. Iron may also be precipitated by 8-hydroxy-quinoline ("oxine") in presence of di-carbonic (oxalic, malonic, etc.) acids. 8-Hydroxy-quinoline was introduced as an analytical reagent by Berg in 1927. By varying the conditions under which precipitation is effected, it can be used for the determination of a variety of metals, including aluminium. It has the advantage that the compound with aluminium, $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$, contains only 5.9 per cent. of aluminium so that small amounts of the metal can be determined with great accuracy. The precipitate can be weighed or titrated.

Colorimetric methods, depending upon the readiness with which aluminium forms coloured lakes with certain dyes, have been much used. Their accuracy depends largely upon the solution being of just the right degree of acidity, a condition which it is not always easy to secure. If the prescribed methods of working are rigidly adhered to, colorimetric methods are satisfactory, but there is always some degree of uncertainty in them. Myers, Mull and Morrison's (1928) method, as modified by Lampitt and Sylvester (1932), using aurin tricarboxylic acid has given good results in my hands and has the advantage of quickness.

Spectroscopic methods have been used by several workers and are valuable as shewing whether or not aluminium is present in a sample, but quantitative measurements by these methods are approximate only.





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B. Determination of aluminium in foods by 8-hydroxy-quinoline.

The following method for determining aluminium in foods and biological material, depending on precipitation by 8-hydroxy-quinoline, has been worked out in the Foods Laboratory of the Ministry of Health. Although considerably longer than some of the colorimetric methods referred to above, it has the advantages that it is applicable over a wider range of aluminium content and that the aluminium is obtained in a form in which it can be weighed or titrated.

A suitable weight of the sample, usually from 25 to 100 gm., is dried and thoroughly charred in a silica dish. The char is moistened with about 10 ml. of normal sulphuric acid, dried and ashed at a low temperature in a muffle furnace. The sulphated ash is extracted on a water-bath with successive small quantities of dilute hydrochloric acid. If there is an insoluble residue this is filtered off and washed with hot water. The moist filter paper is transferred to a platinum dish, ignited and the residue fused with 0.5 gm. each of pure sodium and potassium carbonates. The fused mass is dissolved in hydrochloric acid and added to the main solution. The combined solution of the ash is evaporated to dryness in a silica dish and the residue heated at 150°C. to dehydrate any silica that may be present. It is cooled and extracted with small quantities of moderately strong hydrochloric acid and the liquid filtered. Iron is oxidised by boiling with a few drops of nitric acid and the solution evaporated to about 20 ml. If there is not sufficient iron present to give the solution a perceptible yellow tinge, one drop of 5 per cent. ferric chloride solution is added. There should also be an excess of phosphoric acid present over that required to combine with the whole of the iron and aluminium. Working on 100 gm. of a sample the addition of 0.1 gm. of ammonium phosphate was usually found to be sufficient.

The solution is transferred to a large boiling tube (8 ins. by 1½ ins.), a few drops of thymol blue solution* added and dilute ammonia run in from a burette until a slight permanent precipitate or turbidity is produced. The solution should still be acid, and red to orange in colour. 3 ml. of glacial acetic acid are added and the liquid brought just to boiling point. The precipitation is completed by the addition of 5 ml. of 50 per cent. ammonium acetate solution. The ammonium acetate should be added to the hot liquid gradually with stirring. The solution, which is now yellow, is transferred to a centrifuge tube, allowed to stand for 5 to 10 minutes, cooled and centrifuged. The supernatant liquid is poured off as far as possible and rejected. The moist precipitate is shaken

* Thymol blue is red in acid solution, changes through orange to yellow at P_H 1.2–2.8 and becomes blue at P_H 8.0–9.6.

up with hot water, cooled and recentrifuged. The liquid is poured off, the mixed phosphates of iron and aluminium dissolved in the least possible quantity of warm dilute hydrochloric acid and the solution diluted to about 15 ml.

The iron is now separated as basic acetate by the addition of 1.25 ml. of glacial acetic acid, followed by 6.5 ml. of approximately 6 N sodium hydroxide solution (free from aluminium). The liquid is allowed to stand for at least half an hour during which time it should be shaken occasionally. It is then centrifuged, and the supernatant liquid poured off into a small beaker. If the residual precipitate of basic iron acetate occupies a volume of more than 0.5 ml. it must be redissolved, precipitated and centrifuged and the supernatant liquids combined.

The alkaline solution containing the aluminium is diluted to about 30 ml. and made just acid to bromothymol blue by dilute acetic acid. If it contains upwards of 0.3 mgm. of aluminium, a turbidity or precipitate of aluminium phosphate usually forms. Powdered tartaric acid is added until any phosphate which may have separated is redissolved. 5 ml. of 50 per cent. ammonium acetate solution are added and the aluminium is precipitated by the gradual addition of a slight excess of 8-hydroxy-quinoline acetate reagent.* Each ml. of this reagent precipitates about 1.4 mgm. of aluminium. If more than 2 ml. is required it is advisable to dilute to 50-60 ml. The solution is neutralised with dilute ammonia, and finally made just acid with dilute acetic acid. The beaker is covered with a watch glass, heated to about 70° C. for 15 minutes, and allowed to stand at room temperature overnight.

The greenish-yellow precipitate is filtered off with suction, washed with small quantities of warm water and dissolved in about 10 ml. of hot hydrochloric acid (4 vols. conc. HCl + 1 vol. water). The solution is cooled and slowly titrated with 0.1 N bromine (bromide-bromate) solution using indigo carmine as indicator, and an excess of 0.5 to 1.0 ml. of bromine solution added. The exact amount of bromine present in excess is determined by adding potassium iodide and titrating the liberated iodine with sodium thio-sulphate and starch.

1 ml. 0.1N bromine = 0.000225 gm. aluminium.

All reagents used, especially the sodium hydroxide, should be the purest obtainable. Blank experiments on the reagents in the quantities used gave 0.00025 gm. of aluminium when fusion with mixed alkali carbonates was necessary and 0.00013 gm. when fusion could be dispensed with. Sodium hydroxide solution should be kept in a bottle the inner surface of which has been waxed.

* The 8-hydroxy-quinoline acetate reagent is prepared by triturating 2.5 gm. of the base with 5 ml. of glacial acetic acid, pouring the mixture into 100 ml. of water at 60°C, cooling and filtering (Lundell and Knowles, 1929).

The results of test analyses carried out with various materials, to some of which known amounts of aluminium had been added, are given in the accompanying table.

	Amount taken for analysis. gram.	Aluminium added.	Aluminium found.
Solution of potassium alum containing 1 mgm. Al.	—	—	0.99 mgm.
Calcium phosphate ..	0.1	0.5 mgm.	0.48 mgm.
„ „ ...	0.1	1.0 mgm.	0.96 mgm.
Bran (as bought) ...	50	—	4.5 parts per million.
„ „ ...	50	20 parts per million	22.95 (=4.5+18.45) p.p.m.
Rice (as bought) ...	100	—	0.45 p.p.m.
„ „ ...	100	10 p.p.m.	10.57 (=0.45+10.12) p.p.m.
Potatoes (peeled) ...	100	—	Nil.
„ „ ...	100	10 p.p.m.	9.2 p.p.m.
Coffee beans (as bought)	25	—	72 p.p.m.
„ „ (washed) ...	50	—	Nil.
Lettuce (washed) ...	100	—	0.34 p.p.m.
„ „ ...	100	10 p.p.m. of lead added	Nil.
Sphagnum moss (washed)	45	—	58 p.p.m.
Lycopodium powder ...	10	—	497 p.p.m.

Under the conditions given above for the precipitation of aluminium and iron phosphates the only other common metals that may, if present, be precipitated with the iron and aluminium are titanium, bismuth, tin and lead. Titanium and bismuth are completely removed with the iron when this is separated as basic acetate. Tin and lead may pass into solution with aluminium in dilute sodium hydroxide solution. Tin is not precipitated by 8-hydroxy-quinoline in weakly acid solution. Lead gives a purple-brown precipitate which is much less insoluble than the greenish-yellow aluminium compound. Thus a solution containing 1 mgm. of aluminium gave a precipitate which on titration required 4.5 ml. of 0.1 N bromine solution, while a solution containing 1 mgm. of lead similarly treated gave only a trace of precipitate and a titration of 0.5 ml. If lead happens to be present in much larger amount than aluminium it must be removed by sulphuretted hydrogen before precipitating the mixed phosphates.

4. THE ACTION OF FOOD ON ALUMINIUM VESSELS.

The figures given by various workers for the amount of metal taken up by food from aluminium vessels vary considerably owing to different conditions of experiment. Distilled water, whether

hot or cold, has practically no action. Hard waters, on the other hand, corrode aluminium slightly and may become cloudy with suspended aluminium hydroxide. The amount thus taken up by water is of the order of one to five parts per million (Lehmann 1929, Massatsch and Steudel 1930, Lampitt and Sylvester 1932), although occasionally it may rise to 25 parts per million, as for instance when hard water is evaporated to a small bulk in an aluminium vessel (von Fellenberg 1928). According to Thieme (1929) alkalinity in water favours corrosion of aluminium. In some experiments carried out for this Report, distilled water was boiled in aluminium saucepans and allowed to stand overnight. The vessels were unaffected and no aluminium could be detected in the water. A similar experiment carried out with tap water in five different aluminium saucepans gave 7.7, 15.1, 15.6, 18.0 and 19.2 parts of aluminium per million respectively.

Organic acids act on aluminium to some extent, especially when dilute, and acetic acid appears to act more strongly than tartaric, lactic or citric acids. Lunge and Schmidt (1892) found that aluminium sheets immersed in acetic, citric and lactic acids at strengths from 1 to 5 per cent. for six days at room temperature lost from 2 to 5 mgm. in weight. Lehmann (1929) found that acetic acid of 0.6 per cent. strength, boiled for three hours, took up 24 parts of aluminium per million, while acid of 0.5 per cent. and 2 per cent. strength, boiled for six hours, took up 58 parts per million. Ohlmüller and Heise (1893) boiled "dilute" nitric acid for half an hour in aluminium and found that it took up 130 to 170 parts per million.

The action of acids when present in foods appears to be much less than that of the pure acids alone. Friend and Vallance (1922) drew attention to the effect of colloids in preventing the corrosion of aluminium. The addition of 0.1 per cent. of gelatine reduced the rate of corrosion to one half. This action of colloids probably accounts for the fact that sour milk, containing about 0.7 per cent. of lactic acid, has only a slight action on aluminium, and that "sauerkraut", with an acidity equivalent to 1.4 per cent. of lactic acid, when cooked in aluminium takes up less than 5 parts per million. Lampitt and Sylvester (1932) found that tomato soup took up 9 parts per million and apples cooked with sugar and water 12 parts, while von Fellenberg (1928) found only 1.6 parts per million in apples similarly cooked. Tomato salad allowed to stand in aluminium for 18 hours took up only 1.6 parts per million (Lehmann 1931). Beal and others (1932) found that vegetables cooked with carbonate of soda in aluminium vessels took up about 90 parts per million.

In some experiments carried out for this Report a mutton broth containing mixed vegetables was cooked in an aluminium pan. After being sampled it was allowed to remain in the pan and

reheated on successive days. A similar mixture was cooked in an enamelled pan as a control. The results were as follows:—

	<i>Aluminium in parts per million of broth.</i>			
Cooked in enamelled pan				1.13
Cooked in aluminium pan—				
i. Immediately after cooking				7.0
ii. After 24 hours				10.6
iii. After 48 hours				11.5

Salt is commonly supposed to favour the corrosion of aluminium, but von Fillinger (1908), Lehmann (1929) and von Fellenberg (1928) found that pure salt solutions, even when boiling, had very little action. Bryan (1935), in an investigation on the suitability of aluminium for canning, found that corrosion by salt is slight in neutral solutions, but is greatly increased in the presence of citric acid. The higher the acidity the greater is the corrosive action of salt.

The degree of purity of the metal may have some influence on its liability to corrosion. Much of the older work was carried out with aluminium containing considerable amounts of iron and silicon, and it would appear that the purer the metal the more resistant it is to corrosion. Commercial aluminium of 99.5 per cent. purity can now be produced; it is more homogeneous than formerly and not so liable to corrosion from local electrolytic action.

Wesley (1932) states that if aluminium comes into contact with nickel, copper or stainless steel it becomes anodic and corrodes more readily, but according to Wührer (1932) anodic oxidation may, in certain circumstances, be of advantage in forming a thicker film of oxide on the surface and thus protecting the metal. Several authors have drawn attention to the fact that corrosion of aluminium vessels becomes less during prolonged use and tends to reach a minimum, owing apparently to the formation of a resistant oxide coating. A process is, in fact, in operation for increasing this oxide coating to a thickness of 0.01 to 0.04 mm. by anodic oxidation (Elssner 1935).

A brown or black deposit often forms upon aluminium vessels during use, especially when hard water is boiled in them. According to Formenti (1905) this deposit is graphitic silicon, but Tinkler and Masters (1924) found it to consist almost wholly of finely divided iron left behind on the surface when aluminium is removed by corrosion. The stain is readily removed by weak acids and is not produced if the aluminium is previously treated in such a way as to increase the thickness of the oxide film.

Aluminium is readily acted on by alkalies, and cooking utensils are therefore liable to be damaged if cleaned too often with soda. The addition of a small proportion of sodium silicate prevents corrosion by sodium carbonate (Seligman and Williams 1922).

5. BEHAVIOUR OF ALUMINIUM IN THE BODY.

The problem of whether or not aluminium is injurious in moderate doses involves a number of different questions. Is it, for instance, absorbed into the blood stream from the digestive tract; if so, does it affect the blood in any way, such as by causing anaemia; is it carried by the blood to any of the organs and there deposited, and if so does it affect their functions and has it any ultimate effect on growth or reproduction; is it excreted by way of the liver with the bile into the intestine, or by the kidneys into the urine; is it irritant, corrosive or astringent to any part of the digestive tract; can it interfere with the normal processes of digestion or affect the availability of phosphoric acid or any other food constituent; and is there any evidence of idiosyncrasy or individual hypersensitiveness to aluminium?

Much of the work which has been undertaken on these questions has been in connection with alum baking powders. As ordinarily used, baking powders prepared with sodium aluminium sulphate may introduce into bread about 0.05 per cent. of aluminium or 500 parts per million. This is much more than the amount taken up by food from aluminium cooking vessels, even allowing for the fact that bread usually forms only a small part of a mixed diet, whereas a large proportion of the daily food may have been cooked in aluminium vessels.

A. Solubility in gastric juice.

The state of combination in which aluminium may exist in the stomach contents is largely a matter of conjecture and probably varies with different conditions. Aluminium in the form of hydroxide or phosphate is readily soluble in weak hydrochloric acid and presumably goes into solution in the gastric juice. On the other hand salts of aluminium are precipitated by proteins in weakly acid solutions (Maillard and Wünschendorff 1926), so that in the presence of a large amount of food, aluminium may be partially or wholly held in combination with organic matter until this has been digested. Pitkin (1887) found that when gastric juice, obtained from a dog with a gastric fistula, was allowed to act upon biscuits baked with alum baking powder about one-third of the aluminium was rendered soluble. Myers and Killian (1928) describe experiments on hospital patients fed with biscuits made with alum baking powder, in which the stomach contents were withdrawn and analysed. They found that the amount of aluminium passing into solution was extremely variable, from 6 to 54 per cent. of the amount actually present. The quantity in solution bore no relation to the degree of gastric acidity. Schaeffer and others (1928) in similar experiments found that about one-third of the aluminium administered went into solution, the remainder being absorbed by solids present in the stomach, but the results were variable and difficult to interpret, owing to the constant passage of the stomach contents on to the further regions of the digestive tract.

It may be concluded, therefore, that a considerable proportion of the aluminium taken into the stomach is soluble, the actual amount dissolved varying greatly with circumstances.

B. Absorption into blood stream.

Much of the controversy on the subject of aluminium, as indeed of metals generally, is centred on the question whether it is able to diffuse through the walls of the intestinal tract and get into the blood. Experimentally, this problem has been attacked in several ways :—

- (i) By direct determination of aluminium in the blood.
- (ii) By making haemoglobin determinations and blood counts after administration of aluminium.
- (iii) By ascertaining whether aluminium is excreted in the urine.
- (iv) By experiments on the permeability of living membranes to aluminium salts.
- (v) By determining the amount of aluminium in the organs of the body after prolonged feeding experiments.

(i) *Aluminium in the blood.*

Underhill and Peterman (1929) carried out experiments on the amount of aluminium in the blood of dogs before and after the consumption of bread made with alum baking powder, and found that there was slight but definite absorption of aluminium. The amount normally present in blood was 2 to 3 parts per million, and this rose to 5 or 6 parts during the experiments.

With human blood the results were doubtful; sometimes there was a slight increase of aluminium, sometimes not. If the subjects were put on a diet as free as possible from aluminium, the aluminium in the blood showed a definite fall. Judd Lewis (1931), using a delicate spectroscopic method, found that normal blood contained no aluminium, but that on a daily diet of 0·09 grm., in the form of baking powder scones, aluminium quickly appeared in the blood to the amount of about 1 part per million. Its presence could be detected even after one meal.

Mackenzie (1932) injected aluminium tartrate into the ligatured intestine of a rabbit, and found traces of aluminium, less than 1 part per million, in the blood. He concluded that although aluminium may in certain circumstances be absorbed from the intestine the amount thus conveyed into the blood stream is insignificant.

(ii) *Anaemia.*

Siebert and Wells (1929) state that rabbits consuming 0·1 grm. of sodium aluminium sulphate (11 mgm. of aluminium) daily in their food eventually showed less haemoglobin in their blood than control rabbits receiving no aluminium. From the charts which they give in support of their statement it is difficult to say definitely

whether aluminium had any effect on the rabbits. Siebert and Wells seem to have obtained rather more definite indications by giving the rabbits large doses of aluminium acetate, metallic aluminium and precipitated hydroxide, but even here the results were erratic and it is doubtful whether the interpretation placed on them by the authors is correct. The United States Referee Board (1908) had previously carried out extensive blood tests on groups of men on a diet high in aluminium, and in no cases were they able to detect any diminution in the amount of haemoglobin or any signs of degenerative changes in the blood corpuscles. Waltner and Waltner (1929), in the course of a series of experiments on the effect of large doses of metals and their salts upon bone formation and blood production, found that when rats were fed for several weeks upon food containing 2 per cent. of metallic aluminium, neither growth nor bone formation were affected, but there was a decided decrease in the number of red corpuscles and in the haemoglobin content of the blood. Mitchell and Miller (1931), in experiments upon nutritional anaemia, found that salts of aluminium, when added to an anaemia-producing diet, had no effect on the animals. Scott and Helz (1932) could find no changes in the blood of rats fed for long periods on a grain mash to which 0.4 per cent. of aluminium, in the form of chloride, had been added. Two of the rats did show a slightly low haemoglobin content and red cell count, but the figures were held to be within the limits of normal variation.

Flynn and Inouye (1928) have discussed the question of anaemia due to metals in food and suggested that metals may possibly combine with constituents of the blood cells or serum and affect some of their functions such as those of resistance to disease, although no apparent effect on blood haemoglobin or morphology can be detected. This is a difficult line of investigation, but it would seem that it might repay further study, from the view-point not only of aluminium but of metals in general. It is well known that aluminium, even in traces, can combine with certain organic substances in solution as shown by the formation of "lakes" with soluble colouring matters, a reaction which is the basis of several analytical methods. It is conceivable that extremely small amounts of aluminium, gaining access to the blood, might immobilise or affect adversely some constituent which operates normally in resisting disease. This is at present pure surmise, but it indicates one important aspect of the biochemistry of metals which awaits further study.

(iii) *Excretion in urine.*

If aluminium is excreted in urine this is direct evidence of its presence in the blood. Its absence in the urine does not however imply its absence in the blood, as it may have been excreted in other ways, for instance, through the liver and bile into the intestinal tract.

Mackenzie (1931), in experiments on pigs, could find no evidence of aluminium being excreted in the urine. Wührer (1933), in experiments on dogs and on human subjects with the administration of aluminium in amounts up to 0.6 gm. daily, could find no increase in the amount excreted in the urine. The amount so excreted varied from nil to 0.15 mgm. Underhill and Peterman (1929), in experiments with men, found that the urine passed in 24 hours (about $1\frac{1}{2}$ litres) seldom contains more than 0.5 mgm. of aluminium, and that this is increased slightly after consumption of food containing aluminium. In the experiments carried out for the United States Referee Board in 1908, no aluminium could be found in the urine of any of the subjects.

(iv) *Permeability experiments.*

For aluminium to be absorbed into the blood stream it must be capable of passing by dialysis through the colloidal membranes of the stomach or intestines.

Kärber (1933) carried out experiments upon the skins of freshly killed frogs with aluminium solutions of varying strengths. He found that only in the case of strong solutions ($M/5$ to $M/2$), strong enough to cause definite changes in the character of the membrane, was there any considerable transfusion of aluminium. With weak solutions only traces of aluminium passed through. In experiments with the intestines of cats under urethane narcosis the gut wall was not completely impermeable to aluminium salts, but allowed their passage in extremely small amounts. These results are in agreement with the finding of traces of aluminium in almost all human and animal tissues and organs. It is, perhaps, hardly to be expected that any natural membrane can be absolutely impermeable to a metallic salt.

Absorption from the intestinal tract may be promoted by certain substances. Bile is specially active in this respect (Langecker 1928) and saponins also have the effect of increasing diffusion of some substances (Kofler and Fischer 1929) although not, apparently, of aluminium (Kärber 1933). Kärber found that in presence of urea the diffusion of aluminium was increased, while extract of gall also had a slight action. It would seem likely that the diffusibility of aluminium salts into the blood through the wall of the digestive tract may vary appreciably with circumstances and with the nature of the stomach contents.

(v) *Aluminium in organs of the body.*

According to Underhill and Peterman (1929) aluminium feeding, although it may increase the aluminium content of the blood, does not affect that of the various organs, that is to say aluminium is not retained in the body but excreted as fast as it is absorbed. Wührer (1933) also could find no increase of aluminium in the various organs of dogs after the administration, over a long period, of daily doses up to 1 gm. of precipitated aluminium hydroxide mixed with food. On the other hand Myers, Mull and Morrison

(1928) found that the aluminium in rats' and dogs' livers was appreciably increased by aluminium feeding. The normal amount of 1.5 parts per million in dog's liver rose to 2.7 parts per million. Mackenzie (1930) found that pigs consuming 1 gm. of aluminium daily in their food showed an increase of about 5 parts of aluminium per million in their livers. Leary and Sheib (1917), feeding the equivalent of 0.1 to 0.3 gm. of aluminium daily to puppies and young rats, obtained evidence of an increase of aluminium in the organs, especially the liver. Gonnermann (1920) found aluminium in gall stones but this must be regarded as exceptional.

Wührer found it difficult to determine small amounts of aluminium in bones, owing to the large amount of calcium present, but approximate determinations indicated that aluminium is not deposited in bones.

A possible source of aluminium in the body, apart from food, is atmospheric dust, which is constantly entering the lungs. Dogs show a progressive increase of aluminium in their lungs with age. Underhill and Peterman found over 50 parts per million in the lungs of a dog aged 15 years and 14 parts per million in its liver. Presumably any insoluble aluminium silicate entering the lungs in the form of dust would remain there and not find its way into the blood.

C. Effect on digestive tract.

A long series of experiments was carried out for the United States Referee Board appointed in 1908 to consider the question of alum baking powder. Squads of men were placed on diets containing 0.06 to 0.26 gm. of aluminium daily in the form of baking powder, and in one series of experiments still larger amounts, up to 0.97 gm. of aluminium for short periods. It was found that large doses of alum baking powder and the residues from baking powder produced gastro-intestinal irritation with colic, while small doses, such as would normally be consumed in bread, had no apparent effect. This action of baking powder was attributed almost entirely to the sodium sulphate which is one of the chief constituents of the residue, although the aluminium component was admitted to be responsible for a certain amount of colic in large doses. These experiments are not very convincing. The medical records of the different subjects of the experiments, with details of various symptoms which appeared at different times, hardly bear out the contention that they all started in perfect health and remained so for the period of the experiments. It is difficult to avoid the conclusion that in these, as in most similar experiments carried out on squads of volunteers, it is only the grosser and more obvious effects of a particular substance which can be satisfactorily investigated, and that the finer points are likely to be obscured by a host of variable factors. The results merely show that aluminium compounds, in reasonable doses, do not make the normal person obviously ill within a period of weeks or months.

Schaeffer and his co-workers (1928) carried out a long series of experiments on animals with bread prepared with alum baking powder. They gave large doses, proportionately more than the highest given in the Referee Board experiments. Dogs were fed with 50 gm. of bread containing altogether 1.2 gm. of aluminium, i.e. about five times as much as is normally present in bread prepared with alum baking powder. The dogs were killed at intervals of 4 to 7 hours after the meal, their stomach contents collected, and the extent of digestion compared with that of controls receiving no aluminium. The amount of undigested bread found in the stomachs of the dogs that had received aluminium was nearly twice as great as in those of the controls. Gastric evacuation was delayed and eventually diarrhoea was produced. The effects were not due to sodium sulphate since they were produced also by aluminium oxide and phosphate. Prolonged feeding on alumed bread led to well-defined lesions of the large intestine. In mice fed on a similar diet gastric lesions were observed.

Wührer (1934) fed dogs on a daily ration containing (i) 0.18 to 0.36 gm. of aluminium in the form of potassium alum, (ii) 0.36 gm. of aluminium in the form of sulphate, and (iii) 0.07 to 0.13 gm. in the form of aluminium acetate. The dogs showed no ill effects even after several weeks on this diet, but there was a "loss of appetite due to the local astringent and partly corrosive action of these large amounts of strongly dissociated aluminium salts". In a series of experiments with precipitated aluminium hydroxide administered with food to dogs for several months in daily doses up to 0.5 gm. of aluminium daily, no apparent symptoms were produced. Daily administration of 0.03 gm. of aluminium in the form of chloride for several months also produced no apparent symptoms in dogs. With men there was no discomfort after a meal containing 0.5 gm. of aluminium in the form of precipitated hydroxide, but consumption of half this quantity daily over a period of 70 days led to a transitory feeling of heaviness in the stomach towards the end of the period.

Colloidal aluminium hydroxide has been administered with success as an ant-acid in doses of about 1 gm., and it is stated to be particularly useful in cases of gastric and duodenal ulcers. It reduces acidity either chemically or by physical adsorption of hydrochloric acid by the colloidal particles, without producing alkalinity. Thieme (1929) states that it has occasionally been administered in doses of several grammes for intestinal worms.

D. General effect on health, growth and reproduction.

Mackenzie (1930, 1931), feeding pigs and rats on food containing aluminium in the form of sodium aluminium sulphate, could observe no ill effects. All the aluminium was excreted in the faeces. His pigs received 0.8 to 1.4 gm. of aluminium daily, which is roughly the same amount as Schaeffer gave to his dogs.

Schaeffer's dogs, however, received it in a meal of 500 gm. of bread, while Mackenzie's pigs apparently had it incorporated with the daily food ration, which cannot have been much less than $3\frac{1}{2}$ to $4\frac{1}{2}$ pounds of dry food for each pig. The percentage of aluminium calculated on the dry food is 0.34 in the case of Schaeffer's dogs and from 0.05 to 0.10 in the case of Mackenzie's pigs. Perhaps it is hardly to be expected that food containing 0.05 per cent. of aluminium, an amount not greater than is present in bread baked with the normal amount of alum baking powder, would have a perceptible effect on pigs. In many of these records of feeding experiments it is difficult to compare the results owing to lack of information of the amount of food eaten by the animals daily or at a meal. Possibly it is the concentration of aluminium in the stomach contents at any given time, rather than the total quantity consumed, that determines whether or not it has any injurious action.

Schaeffer (1928) fed young rats, chickens and mice for prolonged periods on bread containing 0.3 per cent. of aluminium, which is about six times the amount normally present in bread prepared with alum baking powder. The bread formed the major part of a carefully adjusted mixed ration. Appreciable differences appeared in the growth curves. He concluded that growth is retarded in proportion to the amount of aluminium present and that the younger the animals the more they are affected. The older animals did not appear to be affected. Prolonged feeding with these high amounts of aluminium was found to have a decided effect on reproductive capacity, due apparently to atrophy of the ovaries. Schaeffer considers this to be the most specific and characteristic action of aluminium.

Scott and Helz's (1932) results are at variance with Schaeffer's. These investigators fed rats for long periods on a grain mash to which 0.4 per cent. of aluminium, in the form of chloride, had been added. No adverse effect on growth, reproductive capacity or condition of the blood was observed. The rats were from three to four weeks old and weighed 40 gm. when the experiments were started, while Schaeffer's rats, the growth of which was found to be affected by aluminium feeding, were six weeks old and weighed from 70 to 80 gm. Mackenzie (1932) found that reproduction in rats was not affected, but the amount of aluminium given in his experiments was less than that given by Schaeffer.

Myers and Mull (1928) state that aluminium has no effect on reproduction, but as they gave their rats the equivalent of only 2 mgm. of aluminium a day, it is hardly to be expected that they would observe any effect on the rats. Steudel (1932), also administering very small amounts of aluminium, could find no effect on reproduction in rats. Plagge and Lebbin (1893), gave rabbits 0.1 to 0.2 gm. of aluminium daily for two months and could observe no ill effects.

Leary and Sheib (1917), administered 0·1 to 0·3 gm. of aluminium daily to puppies and young rats in their food and could observe no adverse effect on their growth. Evidence was obtained, however, that a certain amount of phosphoric acid was made unavailable, and was excreted in the faeces. This question of immobilisation of phosphoric acid, owing to the formation of aluminium phosphate, has been raised by various authors. In certain of the experiments carried out for the United States Referee Board indications were obtained that aluminium causes a decrease in urinary phosphoric acid and a corresponding increase in faecal phosphoric acid. On the other hand Mackenzie (1931), could find no diminution of phosphoric acid in the urine of pigs on a diet containing aluminium.

E. Results of injection of aluminium salts into the body.

Underhill, Peterman and Steel (1929), found that aluminium, when injected intravenously, appeared in the bile and urine, and that some of it was stored in the tissues. Intravenous injections of 0·7 gm. of sodium aluminium sulphate (corresponding to 0·08 gm. of aluminium) into a rabbit killed it (Siebert and Wells 1929). Daily injection of smaller quantities (1 to 2 mgm. of aluminium) caused definite anaemia, but whether this was due to the aluminium, or to the other constituents of the sodium aluminium sulphate, is not clear. According to Siem (1886), the lethal dose of sodium aluminium tartrate, when injected repeatedly over a period into animals, is about 0·12 gm. per kgm., but it is questionable whether much of this toxicity may not be due to the tartrate component (Pearce and Ringer 1913). Myers and Mull (1928), found that aluminium injected intraperitoneally was carried by the blood to the liver. Aluminium salts when injected into the body appear to have much the same degree of toxicity as iron salts (McGuigan 1927, Bertrand and Serbescu 1931).

The results of injection experiments, while valuable in giving information, on the purely scientific side, about the behaviour of substances in the body, cannot be adduced as evidence of toxicity when the substances in question are taken by the mouth.

6. CLINICAL OBSERVATIONS AND EXPERIENCE.

A few medical practitioners have recorded cases in which trains of symptoms have been diagnosed as being due to aluminium poisoning set up or aggravated by the consumption of food cooked in aluminium vessels (Le Hunte Cooper 1932, Spira 1933). According to Spira the symptoms fell into three main groups, gastro-intestinal, cutaneous and general, and Le Hunte Cooper gives full details of cases presenting gastro-intestinal and rheumatic symptoms. All the cases showed marked improvement when cooking in aluminium vessels was discontinued. Burn (1932) criticises these statements severely and attributes the improvement observed in the patients

solely to psychological causes. Whether this criticism is justifiable or not, experience shows that it is often very difficult to assess the value of clinical evidence or to relate clinical observations with certainty to any particular cause. It is conceivable that certain people may possess an idiosyncrasy towards aluminium similar to that shown to certain other substances, but if such a condition is suspected a responsibility rests upon the observer to investigate the possibility in such a way as will not leave the conclusion open to doubt. It cannot be said that available evidence indicates the harmfulness to consumers in general of the small amounts of aluminium which may normally be derived from aluminium cooking vessels, but if in any particular individual it could be satisfactorily established that an idiosyncrasy to the metal existed, the prudent course for such an individual would be to avoid it for the future.

7. CONCLUSIONS.

Much of the experimental work which has been carried out to ascertain whether aluminium in food is harmful or not is conflicting and inconclusive. On the general question of the possible effect of very small amounts of metallic salts in the blood and tissues of the body judgment must be suspended until more definite knowledge is obtained. Aluminium salts, in doses which are not unreasonably high, have been shown to be not without action on digestive processes. It is a safe rule to exclude from food as far as possible anything which may reasonably come under suspicion of causing harm and on this account it is undesirable to admit aluminium in the relatively large amounts in which it may be employed as a constituent of baking powders or self-raising flour.

There is, however, no convincing evidence that aluminium in the amounts in which it is likely to be consumed as a result of using aluminium utensils has a harmful effect upon the ordinary consumer. It is possible that there may be individuals who are susceptible to even such small doses of aluminium as may be derived from aluminium utensils, but evidence of this is inconclusive.

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